HALL EFFECT AND CONDUCTIVITY OF SYNTHETIC RUTILE SINGLE CRYSTALS AND SOME ALKALINE EARTH TITANATES

By

MAXWELL CLAYTON ANDREWS

B.S., University of Missouri, 1947
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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The electrical conduction properties of six alkaline earth titanates, Mg_2TiO_4, $MgTiO_3$, $MgTi_2O_5$, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$, have been studied by means of conductivity measurements of the Hall effect on sintered rectangular bars which had been reduced in varying amounts by heating in a suitable atmosphere. The bars of all of the titanates except $BaTiO_3$ were made from powders prepared from compounds of reagent purity. The bars of $BaTiO_3$ were cut from ceramic blocks of the commercially available material. Since TiO_2 is a component used in the formation of the titanates and since the structure consisting of a Ti^{+4} ion surrounded octahedrally by O^{--} ions is common to rutile TiO_2 and to most of the titanates, similar measurements were made on synthetic rutile single crystals in varying states of reduction. These crystals, also in the form of rectangular bars, were cut with the c axis parallel to one of the sample edges.

Some qualitative results regarding the diffusion of the lattice

defects introduced by reduction are given for rutile. In this connection it was observed that the preferred direction of diffusion was along the c axis.

The conductivities of unreduced samples were measured over the temperature range from 20°C to about 500°C while the measurements on the reduced samples were carried out at temperatures from 20°C to -195°C. The resistivities encountered varied from about 0.1 ohm cm. to about 10^{15} ohm cm.

Sample resistances as high as 10^{17} ohms were measured by means of a specially designed vacuum tube electrometer which is described. A relatively simple resistance furnace temperature controller which is capable of holding the temperature variations to less than 0.1°C is also described.

The Hall effect measurements were made by a d-c method and some of the measurements were repeated using an a-c method. The results indicate that the Ettingshausen effect was less than the experimental error.

The impedances of some of the samples were measured as a function of frequency up to 30 megacycles and the results are interpreted as being due to intergranular contact resistances. It is thus shown that d-c resistivity measurements on sintered

bodies do not give the resistivity of the individual grains.

The ionization energies of the donors introduced by reduction in all of the materials investigated are given and the variations of these quantities with the concentration of donors are shown to conform to those described by Pearson and Bardeen for silicon; i.e., the ionization energy is reduced below that existing at infinite dilution by an amount proportional to the cube root of the donor density.

The energy gaps between the highest filled bands and the conduction bands have been determined from resistivity measurements on unreduced materials in the range of intrinsic conductivity.

In some of the more highly reduced samples it was possible to weigh the amount of oxygen removed by the reduction process and thus calculate the corresponding donor densities. In these cases the mobilities were determined approximately from the resistivity data and are compared with the mobilities determined from the Hall effect measurements. Typical values of the latter in cm^2/volt sec. are as follows: Mg_2TiO_4, 0.04; $CaTiO_3$, 0.3; $SrTiO_3$, 3.0; $BaTiO_3$, 0.1; TiO_2, 0.2. The accurarcy of these results was limited by the accuracy of the measured Hall voltages

which were of the order of a few microvolts. In many cases thermal fluctuations and semi-conductor noise completely masked the Hall voltage so that mobility determinations could not be made.

VITA

Maxwell Clayton Andrews was born on September 2, 1925 in McGrann, Pennsylvania. He graduated from Brooklyn Technical High School in Brooklyn, New York in 1942 and entered the United States Navy in 1943. In 1944 he was assigned to the V-12 Officer Training Program under which he attended Purdue University, Lafayette, Indiana, Central College, Fayette, Missouri and the Rice Institute, Houston, Texas. After his discharge he attended the University of Missouri and received the Bachelor of Science degree in Electrical Engineering in August of 1947. In the fall of 1947 he began his graduate work at the University of Illinois where he held a teaching assistantship from October, 1947 to June, 1949, and a research assistantship from June, 1949 to August, 1952.